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Cobalt charge states in sodium cobaltates at intermediate dopings

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ABSTRACT

A likely crucial parameter in explaining the peculiar magnetism of Na_xCoO_2 cobaltates in their paramagnetic state is their charge and spin states in the cobalt layers, responsible for the electronic properties. We examine here the situation for $0.50 \leq x \leq 0.62$, for which it is shown that an increasing amount of Co^{3+} ions appears among ~3.5+ ions for increasing x. Together with our previous results, this defines two regions in the phase diagram, with homogeneous Co states for $x \leq 0.5$ and heterogeneous states for $x > 0.5$. The links with the sodium structural ordering and the nature of magnetism are discussed.

1. Introduction

Sodium cobaltates have recently attracted considerable attention following the discovery of hints of strong correlations [1] and of superconductivity [2]. The latter is remarkable as cobaltates feature a layered structure, reminding one of the high-temperature superconducting cuprates, with layers of edge-sharing CoO_6 octahedra separated by layers of Na ions. On changing the sodium content x, one changes the doping in the Co layers. In a naive picture, going from $x = 0$ to $x = 1$ results in a progressive replacement of Co^{4+} ions (magnetic, $S = 1/2$) with Co^{3+} ions (nonmagnetic, $S = 0$). One would thus expect reduced magnetism as x is increased, which is not what is observed experimentally. Indeed, except for the band-insulator limit $x = 1$ where we have verified the nonmagnetic 3+ state of all cobalts [3], magnetic correlations are ubiquitous, with a crossover at $x^* \sim 0.6$ from a high x weakly-ferromagnetic itinerant behavior to a low x antiferromagnetic correlation regime [4,5].

A crucial point to explain this behavior may be the actual cobalt charge and spin states in the system. Previous results by us showed that there is charge disproportionation for $0.67 \leq x \leq 0.75$ [5], while it is absent for $x \leq 0.5$ [6,7]. Here we focus on the $0.50 \leq x \leq 0.62$ intermediate doping region, which we studied extensively, especially in terms of magnetic correlations in [4]. We show there is heterogeneity of the cobalts states, with increasing amounts of Co^{3+} ions among ~3.5+ ions for x increasing above 0.5. The latter is thus a threshold for charge disproportionation but does not coincide with the above-mentioned threshold $x^* \sim 0.6$ between correlation regimes, and is argued to be linked to the Na ordering.

2. Results and discussion

To establish the different Co states present for $0.55 \leq x \leq 0.62$, we performed ^{59}Co (spin I = 7/2) nuclear magnetic resonance, taking advantage of its sensitivity to the local magnetic and charge environment of Co nuclei (see [4] for experimental details). While spectra obtained at low temperature seem to indicate that the ~3.5+ Co sites detected for $x = 0.5$ are still present (not shown), we notice the presence of a new cobalt NMR signal (left panel of Fig. 1): upon increasing x above 0.5, a set of quadrupolar satellites (marked with stars) develops on each side of the central resonance line. The corresponding Co sites have a resonance much less temperature-dependent than the ~3.5+ sites, with isotropic NMR shift values stable around 2%, and also with a slower transverse relaxation rate. These are the fingerprints of the Co^{3+} site in the $x = 1$ and $x = 0.67$ phases [3,8], showing that such sites start appearing beyond $x = 0.5$.

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